

A Multiresponsive Calix[6]arene Pseudorotaxane Empowered by Fluorophoric Dansyl Groups

Leonardo Andreoni,^{1,2} Giovanni Mariano Beneventi,^{1,2} Gianpiero Cera,^{*3} Alberto Credi,^{2,4} Arturo Arduini,³ Andrea Secchi^{*3} and Serena Silvi^{*1,2}

¹Università di Bologna, Dipartimento di Chimica "G. Ciamician", Via Selmi 2, I-40126, Bologna Italy

²CLAN–Center for Light Activated Nanostructures, Istituto per la Sintesi Organica e la Fotoreattività, Consiglio Nazionale delle Ricerche via Gobetti 101, I-40129 Bologna, Italy

³Università di Parma, Dipartimento di Scienze Chimiche, della Vita e della Sostenibilità Ambientale, Parco Area delle Scienze 17/A, I-43124 Parma, Italy

⁴Università di Bologna, Dipartimento di Chimica Industriale "Toso Montanari", Viale del Risorgimento 4, I-40136 Bologna, Italy

*gianpiero.cera@unipr.it, *andrea.secchi@unipr.it, *serena.silvi@unibo.it

Keywords: supramolecular chemistry, pseudorotaxanes, molecular machines, calix[6]arene, dansyl unit

In the last two decades, calix[6]arenes have emerged as prominent hosts to devise pseudorotaxanes and mechanically interlocked molecules, due to their versatility and remarkable binding properties.^[1] We report the investigation of a novel dansyl calix[6]arene and of its pseudorotaxane complex with a bipyridinium-based axle (Figure 1). In analogy with parent compounds,^[2] the macrocycle shows a strong affinity towards the bipyridinium and their complex can be disassembled upon reduction of the latter. At the same time, the three dansyl units add new and emerging features to the complex, allowing to: i) signal the state of the system by fluorescence (which is quenched upon association); ii) lower the complexation ability of the host by protonation of the dansyl units; iii) enable photoinduced electron transfer processes, which can be exploited to reduce the guest and therefore disassemble the complex. Overall, the investigated pseudorotaxane is a multiresponsive system which can be controlled by means of three reversible and orthogonal stimuli: the reduction of the guest (electrochemical stimulus), the protonation of the host (chemical stimulus) and the photoinduced reduction of the guest *via* the host (light stimulus).

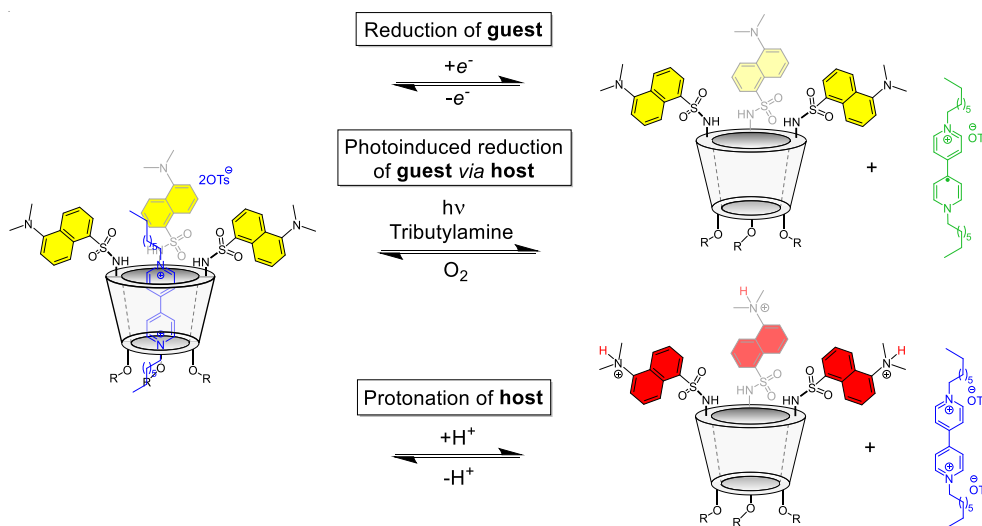


Figure 1. Schematic representation of the calix[6]arene-based pseudorotaxane and its responsiveness to different stimuli.

[1] G. Cera, A. Arduini, A. Secchi, A. Credi, S. Silvi, *Chem. Rec.* **2021**, 21, 1.

[2] A. Credi, S. Dumas, S. Silvi, M. Venturi, A. Arduini, A. Pochini, A. Secchi, *J. Org. Chem.* **2004**, 69, 5881.

This work was supported by the Italian MUR (PRIN 20173L7W8K).